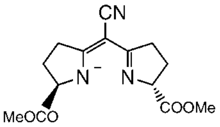
Novel Nickel(II) Complexes for the Catalytic Copolymerization of Ethylene and Carbon Monoxide: Polyketone Synthesis in Supercritical Carbon Dioxide**

Wolfgang Kläui,* Jochen Bongards, and Guido J. Reiß

Polyketone: Suddenly the rush is on.[1] Since 1996 polyketones have been produced industrially as a new class of synthetic materials with superior properties. This was made possible with the discovery of a palladium(II)–phosphane complex that catalyses the formation of perfectly alternating copolymers of CO and olefins at low pressures and temperatures.[2] Since the precious metal remains in the polymer, attempts have been made to use the less expensive nickel as the catalyst metal. So far only a few nickel(II) complexes are known to catalyze the formation of polyketones from CO and ethylene.[3] These systems usually start with the formation of polyethylene; in fact, carbon monoxide initially acts as an inhibitor for the catalysis.[4] Recently, we synthesized the first nickel(II) complex that catalyses the formation of a strictly alternating polyketone of CO and ethylene.[5] This complex was identified by X-ray structure analysis to be [Ni(*o*-tolyl)(PPh$_3$)Tp^{Ph}] (**1**), an aryl–nickel(II) complex with the sterically demanding tris(pyrazolyl)borate ligand Tp^{Ph},[6] which coordinates as a bidentate N,N-chelating ligand to the nickel atom. The mechanism of the catalysis is unknown to date. The crystal structure shows that the hydrogen atom of the borane moiety lies within close proximity of the nickel center. This has led us to hypothesize that a nickel hydride species might initiate the catalytic cycle. However, we were only able to synthesize the closely related compound [Ni(*o*-tolyl)(PPh$_3$)Tp^{pTol}] but none with the ligands Tp, Tp^{Me,Me}, Tp^{tBu}, or Tp^{pTol,Me}. It seemed as if compound **1** was a unique case. We could not determine whether the boron–hydrogen moiety plays a role for the catalytic activity. Now we have discovered that the tripodal ligand Tp^{Ph} can be exchanged for a bidentate N,N-chelating ligand of the semicorrine-type (shown is the anion **2**).[7]



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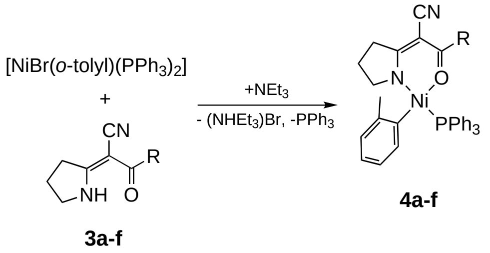
The aryl–nickel(II) complex [Ni(*o*-tolyl)(PPh$_3$)(**2**)] is about twice as active a catalyst as compound **1** for the polyketone formation from ethylene and carbon monoxide. Evidently neither the borane-hydrogen atom nor the tridenticity of the Tp^{Ph} ligand is of any importance for the catalysis. In the development of complexes with the semicorrine ligand, we have discovered a class of N,O-chelating ligands (**3**) that also form aryl–nickel(II) complexes. These new compounds (**4**), which are reported here, catalyze the formation of strictly alternating copolymers from CO and ethylene at low pressures and temperatures with an efficiency that lies orders of magnitude beyond that of all currently known nickel complexes. The novel complexes **4** can be prepared in high yields as shown in Scheme 1.



Scheme 1. Synthesis of the complexes **4**.

The complexes **4** are air-stable, bright yellow solids that give stable aroyl complexes upon reaction with carbon monoxide. In the ^{31}P NMR spectrum of **4d** only one phosphorus peak is detected for the aroyl complex resulting from the insertion of CO into the Ni^{II}–C bond, even after a long period of time and CO pressures of up to 40 bar; no signal for the degradation of the complex to a carbonyl–phosphane–Ni^0 species occurs (the formation of phosphane–Ni^0 complexes is the main termination reaction for the catalysis).

Figure 1 shows the crystal structure of **4d**. The nickel atom is coordinated in a square-planar fashion with the triphenylphosphane ligand in the *trans*-position to the N atom of the chelating ligand.[8] Some of the complexes described here copolymerize ethylene and carbon monoxide with very high efficiencies. While efficiencies for catalysts of type **1** lie at about 170, compounds **4d** and **4e** show efficiencies of up to about 11000 gram polyketone per gram nickel[9] (Table 1).

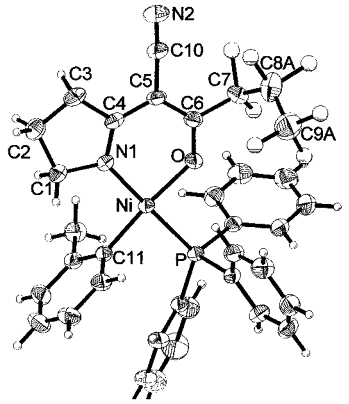


Figure 1. Structure of **4d** in the crystal. For clarity, only one variant of the 1:1 disordered C$_3$F$_7$ group is shown as a ball-and stick model; thermal ellipsoids correspond to 50% probability. Selected bond lengths [Å] and angles [°]: Ni-N1 1.926(2), Ni-O 1.918(2), Ni-P 2.1935(10), Ni-C11 1.893(2), N1-C4 1.299(3), C4-C5 1.438(4), C5-C6 1.387(4), O-C6 1.268(3), C6-C7 1.535(4); O-Ni-N1 91.13(8), O-Ni-P 87.42(6), C11-Ni-P 87.82(8), C11-Ni-N1 93.59(10), N1-Ni-P 177.46(7), C11-Ni-O 175.07(9).

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Table 1. Polymerization efficiencies of **4a–f**.

R	Ligand	Nickel complex	Efficiency[a]
Me	**3a**	**4a**	2000
Ph	**3b**	**4b**	2000
CF_3	**3c**	**4c**	4000
C_3F_7	**3d**	**4d**	11000
C_7F_{15}	**3e**	**4e**	11000
OMe	**3f**	**4f**	0

[a] In gram polyketone per gram nickel.

The catalysis can be performed in dichloromethane, THF, or toluene with approximately the same efficiency, which makes a possible participation of the solvent, for example, by stabilizing a coordinatively unsaturated transition state, improbable.

A striking feature of the catalysis is the great dependency of the efficiency on the substituent R. As shown in Table 1, the best results can be achieved by the introduction of electron-withdrawing groups. In contrast, no polyketone was obtained with compound **4f**. Why perfluorinated side chains have such a positive impact on the catalysis remains the subject for further investigations. It may be possible that the catalyst's ability to stay on the surface of the growing polymer is enhanced with the presence of perfluorinated side chains, thus ensuring the diffusion of ethylene and carbon monoxide. Compounds **4d** and **4e** show almost identical efficiencies. We did not try to further optimize the reaction conditions. Notably, the longer the side chain the more soluble the complexes **4c–e** become in nonpolar solvents. The C_7F_{15} side chain enables complex **4e** to dissolve even in supercritical carbon dioxide ($scCO_2$). First attempts have shown that **4e** catalyses the formation of a strictly alternating copolymer with ethylene and carbon monoxide in $scCO_2$. Numerous polymerization reactions in $scCO_2$ are known to date[10], but to our knowledge the synthesis of polyketones in supercritical carbon dioxide has never been achieved.

The novel nickel(II) complexes reported here show a significantly higher efficiency than all previously reported nickel(II) systems and display a remarkable stability towards carbon monoxide. Thus these catalysts are not dependent on a start of the catalysis by ethylene or low carbon monoxide pressures. Also, for the first time it was possible to perform a copolymerization reaction in supercritical carbon dioxide, which is viewed as one of the solvents of the future for the polymer industry, due to its good dissolving qualities and overall environmental friendliness.[10]

Experimental Section

Ligands **3a–e**: (*E*/*Z*)-(Pyrrolidine-2-ylidene)acetonitrile (1.1 g, 10 mmol)[11] in toluene (100 mL) was treated with NEt_3 (1.0 g, 10 mmol) under an atmosphere of dry nitrogen. After the solution had been cooled to 0 °C, the corresponding acid chloride (10 mmol) was added slowly. The mixture was stirred overnight and the resulting $(NHEt_3)Cl$ filtered off. The filtrate was washed with $NaHCO_3$ solution, separated from the aqueous layer, evaporated, and recrystallized from either diethyl ether or a mixture of diethyl ether/pentane. For example, **3e**: ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 2.28$ (m, $^3J(H,H) = 7.5$ Hz, 2H; CH_2), 3.19 (t, $^3J(H,H) = 8.0$ Hz, 2H; CH_2), (t, $^3J(H,H) = 7.7$ Hz, 2H; CH_2), 10.80 (s, 1H; NH); IR (KBr): $\tilde{\nu} = 3273$ (NH), 2218 (CN), 1628 (C=O), 1581 (C=C); MS(70 eV): *m*/*z*: 504 $[M^+]$, 485 $[M^+ - F]$, 135 $[M^+ - C_7F_{15}]$; elemental analysis (%): calcd for $C_{14}H_7N_2F_{15}O$: C 33.35, H 1.40, N 5.56; found: C 33.50, H 1.35, N 5.61; yield 3.5 g (70 %).

Ligand **3f** was prepared as reported in reference [11].

Complexes **4a–f**: Under N_2 a suspension of $[NiBr(o\text{-tolyl})(PPh_3)_2]$ (2.0 g, 2.7 mmol)[12] and **3a–f** (2.7 mmol) in THF (50 mL) was treated with NEt_3 (2.7 mmol) and stirred for 16 h at room temperature. The suspension was evaporated to 10 mL and the resulting $(NHEt_3)Br$ was separated. The filtrate was evaporated and the resulting solid taken up in small amounts of dichloromethane. The solution was treated with hexanes or methanol, and the complexes **4a–f** precipitated upon evaporation of CH_2Cl_2. Yields 60–85 %. For example, **4e**: ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): $\delta = 1.65$ (m, $^3J(H,H) = 7.9$ Hz, 2H; CH_2), 2.85 (s, 3H; CH_3-tolyl), 2.86 (m, 4H; $2 \times CH_2$); 6.39 (d, $^3J(H,H) = 6.7$ Hz, 1H; tolyl), 6.49 (t, $^3J(H,H) = 7.1$ Hz, 1H; tolyl), 6.56 (t, $^3J(H,H) = 7.2$ Hz, 1H; tolyl), 7.30 (m, 15H; PPh_3, 1H; tolyl); $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 25 °C): $\delta = 26.8$ (s); IR (KBr): $\tilde{\nu} = 2214\ cm^{-1}$ (CN), 1587 (C=O), 1435 (PPh_3); MS(FAB): *m*/*z*: 915 $[M^+ + H]$, 823 $[M^+ - \text{tolyl}]$, 652 $[M^+ - PPh_3]$, 562 $[M^+ - PPh_3 - \text{tolyl}]$; elemental analysis (%): calcd for $C_{39}H_{28}N_2F_{15}NiOP$: C 51.18, H 3.08, N 3.06; found: C 51.10, H 2.92, N 2.90.

General preparation for the synthesis of polyketones: Compounds **4a–e** (0.007 mmol, 4.0–6.5 mg) in 10 mL solvent were transferred into a 100-mL autoclave. The solution was pressurized with 40 bar ethylene and 10 bar of carbon monoxide and stirred with a magnetic stirrer at 60 °C for 16 h. The white solid was filtered off, washed with methanol, and dried. Yields: 0.8–4.5 g; m.p. 260–265 °C; IR (KBr): $\tilde{\nu} = 1693\ cm^{-1}$ (C=O); elemental analysis (%): calcd for $(C_3H_4O)_n$: C 64.3, H 7.2; found: C 64.1, H 7.1.

To monitor the time-dependence of the polyketone formation, the catalysis with **4d** was stopped after 1, 2, and 3 h. The turnover number (TON) was 2300 after 1 h, 2000 after 2 h, and 1800 g polyketone per g nickel per hour after 3 h, corresponding to efficiencies of 2300, 4000, and 5400 g polyketone per g nickel, respectively.

Preparation for the synthesis of polyketones in $scCO_2$: Compound **4e** (5.5 mg, 0.006 mmol) was transferred to a 20-mL autoclave under N_2. The solution was pressurized with ethylene (2.0 g; 40 bar), carbon monoxide (0.4 g; 10 bar) and carbon dioxide (15.6 g), heated to 70 °C, and stirred overnight. The resulting white solid was washed with methanol and dried. Yield: 0.78; m.p. 255–262 °C; IR (KBr): $\tilde{\nu} = 1692\ cm^{-1}$ (C=O); elemental analysis (%): calcd for $(C_3H_4O)_n$: C 64.3, H 7.2; found: C 64.4, H 7.1.

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[8] Crystal structure analysis of **4d**: $C_{35}H_{28}F_7N_2NiOP$, $M_r = 715.27$; crystal dimensions: $0.6 \times 0.7 \times 0.8\ mm^3$, $a = 11.410(2)$, $b = 12.500(2)$, $c = 13.950(3)$ Å, $\alpha = 113.30(3)$, $\beta = 93.90(3)$, $\gamma = 111.30(3)°$, $V = 1649.6(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.440\ Mg\,m^{-3}$, triclinic, $P\bar{1}$. Siemens $P2_1$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite monochromator, $T = 25$ °C, $\Theta_{max} = 28.5°$, $-1 < h < 15$, $-16 < k < 16$, $-18 < l < 18$, 9496 reflections were detected, 8311 independent ($R_{int} = 0.022$), 5779 were classified as observed with $I > 2\sigma(I)$, $\mu = 0.71\ mm^{-1}$, direct methods (SHELXS97), and difference Fourier syntheses (SHELXL97), min-

imizing of $\Sigma w(F_o^2 - F_c^2)$ with $w = 1/[\sigma^2(F_o^2)+0.02P^2+1.1P]$ and $P = (F_o^2+2F_c^2)/3$, 483 refined parameter, $R_1 = 0.0442$, $wR_2 = 0.0953$, $\Delta\rho_{max}/\Delta\rho_{min}$: 0.405 / −0.338 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144043. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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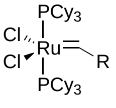
A Soluble Polymer-Bound Ruthenium Carbene Complex: A Robust and Reusable Catalyst for Ring-Closing Olefin Metathesis**

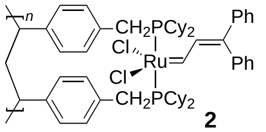
Qingwei Yao*

Facile catalyst separation and subsequent reuse are of prime importance in both industrial and academic settings. From the viewpoint of atom economy,[1] a catalyst should ideally be completely recoverable and reusable. In this respect, immobilized or heterogeneous catalysts offer inherent operational and economical advantages over their homogeneous counterparts. Herein we report the first soluble polymer-bound olefin-metathesis catalyst derived from Grubbs' ruthenium carbene complex and poly(ethylene glycol) (PEG). The new PEG-bound catalyst exhibits remarkable chemical stability and can be repeatedly used and recycled in the ring-closing metathesis (RCM) of a variety of α,φ-dienes.

The enormous recent success of olefin metathesis[2] catalyzed by metal carbene complexes stems from the availability of several well-defined catalysts,[2g] which include the Schrock molybdenum alkylidene[3] and the Grubbs-type ruthenium alkylidenes **1a**[4] and **1b**.[5, 6] Earlier attempts by Grubbs and Nguyen[7] to prepare polystyrene-supported catalysts based on **1a** met with only limited success and the resulting polymer-supported Ru carbene (for example, **2**) was found to be about two orders of magnitude less reactive than the homogeneous analogue **1a**. Moreover, recovery and reuse led to losses in activity (20 % after each cycle). To the best of our knowledge, no further application of this catalyst has been reported in the literature. Very recently, Barrett and co-workers[8] have reported the immobilization of **1b** on vinyl polystyrene. Unfortunately, attempted recycling and reuse of the immobilized catalyst **3** led to a dramatic decrease in activity. The catalyst survives only a limited number of recyclings and completely loses its activity after the third cycle. Therefore, despite the obvious and much desired advantage, development of immobilized ruthenium carbene complexes as active, truly recyclable and reusable catalysts for olefin metathesis remains a challenging task.[9]



1a, R = CH=CPh$_2$
1b, R = Ph



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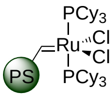

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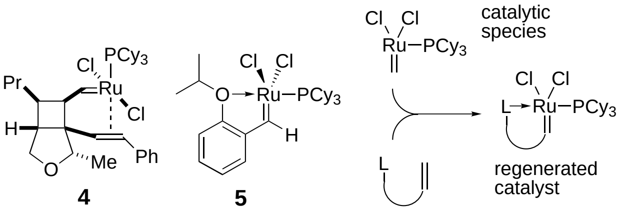
(Cy = Cyclohexyl)

In contemplating a novel approach to the immobilization of metathesis catalysts, we were attracted by two serendipitous findings from the groups of Snapper[10] and Hoveyda.[11] Thus, ruthenium carbenes **4**[10] and **5**[11] (Scheme 1), each bearing one phosphane ligand bound to the metal, were found to be remarkably stable and could be isolated and purified by silica-gel column chromatography. Hoveyda and co-workers also demonstrated[11] that **5** could be recycled by column chromatography and reused in olefin methathesis. Moreover, these complexes catalyze olefin metathesis with greater propagating rates than **1**. The bidentate nature of the non-phosphane ligands is particularly attractive in terms of catalyst regeneration since this should be entropically favored. We expected that attaching **5** to a polymeric support would give a recyclable and reusable olefin metathesis catalyst. We envisioned that it would be advantageous to use a soluble polymer[12] such as poly(ethylene glycol) as the support since this would allow the catalysis reaction to be carried out under standard homogeneous conditions and would enable the simple recovery of the catalyst by precipitation and filtration. However, it was not clear whether the backbone of the polymer would compete with substrate binding by chelating through its multiple ether functionalities.[13]



Scheme 1. Monophosphane-based metathesis catalysts[10, 11] and their regeneration at the end of the reaction.

Starting from the aldehyde **6**, the functionalized styrene **8** was prepared in a straightforward manner (Scheme 2). This material was then coupled to poly(ethylene glycol) monomethyl ether (MeO-PEG) derivatized with a succinate ester

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